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Mesoscale Modeling Framework Design: Subcontract Report

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**Mesoscale Modeling Framework Design:
Subcontract for “Multiscale Capabilities for Exploring Transport Phenomena in Batteries”
(12-ER-053)**

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I. Scope of work

This subcontract is aimed at developing the mesoscale computational capability to help ensure success of the project “Multiscale Capability for Exploring Transport Phenomena in Battery” at the Lawrence Livermore National Laboratory (LLNL). We develop an efficient computer code that implements the smoothed boundary method for simulating charge transport and coupled microstructure evolution in battery electrode architectures.

II. Objectives

- To develop a computational model for solving the governing equations for charge transport in both electrolyte and electrode phases.
- To develop an efficient computer code that implements the smoothed boundary method for simulating charge transport, accompanied phase microstructure evolution, and stress evolution within the polycrystalline electrode upon battery charge/discharge.

III. Progress

- **Modeling diffusional processes near the interface**

One of major components for modeling charge transport is the computational model of the diffusional process of ions or atoms in both electrolyte and electrode. The ionic flux at the interface is determined by the electrochemical reaction taking place at the electrode/electrolyte interface. We have developed the computational model and the corresponding computer code for solving the diffusion equation taking into account a boundary condition imposed at the interface by employing the smoothed boundary method [1].

➤ *Description of the model*

The system is described by the domain parameters (ψ_1, ψ_2) which identify the electrode and electrolyte phases as shown in Fig. 1.

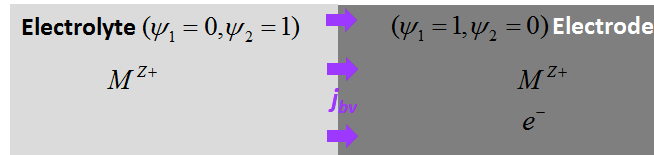


Figure 1. System configuration for charge transport modeling

To integrate the diffusion equation in an electrode with the equation in an electrolyte within a context of smoothed boundary framework, we employ the parameter ($\varphi = \Psi_1^2 + \Psi_2^2$). The derived governing equation is given by the following:

$$\varphi \frac{\partial c}{\partial t} = \vec{\nabla} \cdot [\varphi D(\psi_1, \psi_2) \vec{\nabla} c] + \vec{\nabla} \varphi \cdot \vec{j} \quad (1)$$

where c is the composition, $D(\Psi_1, \Psi_2)$ is a position-dependent diffusivity of the ion, and j is the ionic flux at the interface. The boundary condition ($\vec{j} \cdot \frac{\vec{\nabla} \psi_1}{|\vec{\nabla} \psi_1|} = \frac{j_{bv}}{zF}$ & $\vec{j} \cdot \frac{\vec{\nabla} \psi_2}{|\vec{\nabla} \psi_2|} = -\frac{j_{bv}}{zF}$) was imposed at the interface and the equation becomes:

$$\varphi \frac{\partial c}{\partial t} = \vec{\nabla} \cdot [\varphi D(\psi_1, \psi_2) \vec{\nabla} c] + 2\psi_1 \left| \vec{\nabla} \psi_1 \right| \frac{j_{bv}}{zF} - 2\psi_2 \left| \vec{\nabla} \psi_2 \right| \frac{j_{bv}}{zF} \quad (2)$$

where j_{bv} is the electrical current taking place at the interface and is generally determined by the over-potential at the interface. The equation is numerically solved using the Fourier-spectral method [2].

➤ Preliminary simulation results

Fig.2 shows the preliminary result of the simulation of the diffusional process occurring near the electrode/electrolyte interface as a function of time. We imposed the constant current boundary condition for simplicity and employed the different magnitudes of diffusivity for electrode and electrolyte.

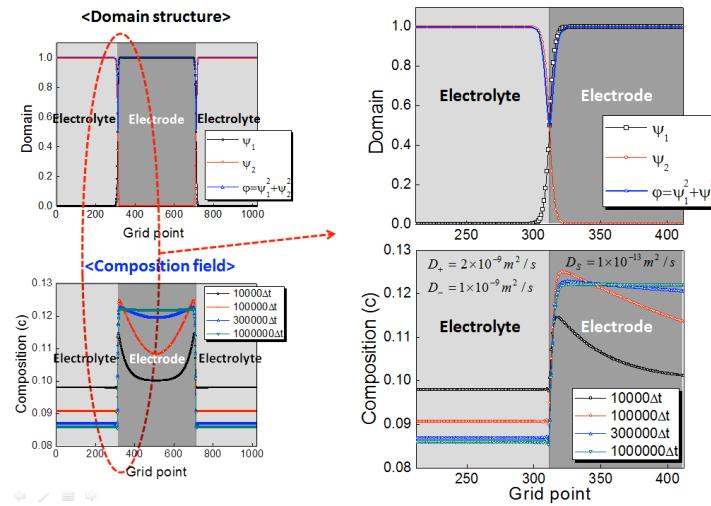


Figure 2. Computer simulations of the diffusional process near the interface

• Calculation of coherency strain energy within an particle

Since the stress evolution during the charge/discharge process influences the kinetics of charge transport itself, the capability of computing the coherency strain energy in a electrode particle is one of key components of charge transport modeling. We have developed the computational model for the calculation of coherency strain energy within a particle with an arbitrary shape by implementing the smoothed boundary method to impose the boundary condition at the surface of the particle.

➤ Description of the model

Since the mechanical equilibrium is usually established much faster than the diffusional processes, we solve the mechanical equilibrium equation. To impose the boundary condition (zero traction force) at the surface of a particle, we employ the smoothed-boundary method [1]. The equation is given by

$$\psi \cdot \left(\frac{\partial \sigma_{ij}}{\partial x_j} \right) = 0 \rightarrow \frac{\partial}{\partial x_j} [C_{ijkl}(\vec{r}) \bar{\epsilon}_{kl}] + \frac{\partial}{\partial x_j} \left[C_{ijkl}(\vec{r}) \frac{\partial u_k}{\partial x_l} \right] - \left[\frac{\partial \psi}{\partial x_j} \right] \cdot \sigma_{ij} = \frac{\partial}{\partial x_j} [C_{ijkl}(\vec{r}) \epsilon_{kl}^0] \quad (3)$$

Employing the boundary condition ($-\left[\frac{\partial \psi}{\partial x_j} \right] \cdot \sigma_{ij} = 0$), the equation becomes

$$\frac{\partial}{\partial x_j} [C_{ijkl}(\vec{r}) \bar{\epsilon}_{kl}] + \frac{\partial}{\partial x_j} \left[C_{ijkl}(\vec{r}) \frac{\partial u_k}{\partial x_l} \right] = \frac{\partial}{\partial x_j} [C_{ijkl}(\vec{r}) \epsilon_{kl}^0] \quad (4)$$

where $\bar{\epsilon}_{ij}$ is the homogeneous strain, u_i is the heterogeneous component of the displacement, ϵ_{ij}^0 is the eigenstrain which represents the lattice mismatch between two different phases (Li-rich (or LiFePO₄) and Li-poor (FePO₄) phases in this case), and $C_{ijkl}(\vec{r})$ is defined as $\psi(\vec{r}) \cdot C_{ijkl}^{ref}$. The elastic modulus mismatch as well as the lattice mismatch between two different phases was considered for the computations. Eq. (4) is numerically solved using the Fourier-spectral iterative-perturbation method [3, 4] since the elastic modulus of the entire system is strongly inhomogeneous.

➤ Preliminary simulation results

Using the proposed equation, we preliminarily tested two different cases of particle shapes: one is a spherical shape particle (isotropic geometry) and the other is a rod shape particle (anisotropic geometry). The particles consist of two different phases (LiFePO₄ and FePO₄).

a. Test geometry 1 (Spherical shape particle): We generated a spherical shape particle and computed the coherency strain energy as a function of crystallographic orientation of phase boundaries and the phase fraction of Li-rich phase by controlling the magnitude of H in Fig. 3. We used the lattice parameters [5] and elastic moduli [6] of two phases as inputs. The computational model can deal with the all the possible crystallographic orientations of phase boundaries inside the particle, and the model allows us to identify the phase boundary orientation producing the least coherency strain energy which is most probable orientation inside the particle.

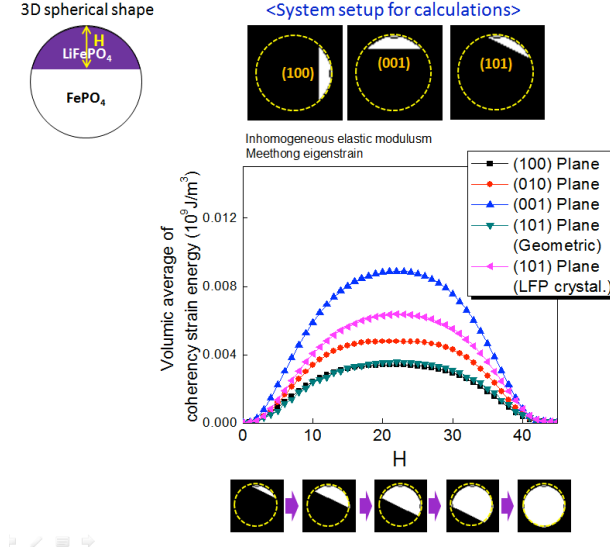


Figure 3. Parametric study of coherency strain energy in a spherical shape particle

b. Test geometry 2 (Rod shape particle): We also tested the rod shape particle consisting of two different phases. We systematically controlled the parameters W and/or L as shown in Fig. 4 and computed the coherency strain energy using the model. This model enables the coherency strain energy calculations with different configurations of phases within a particle of an anisotropic geometry.

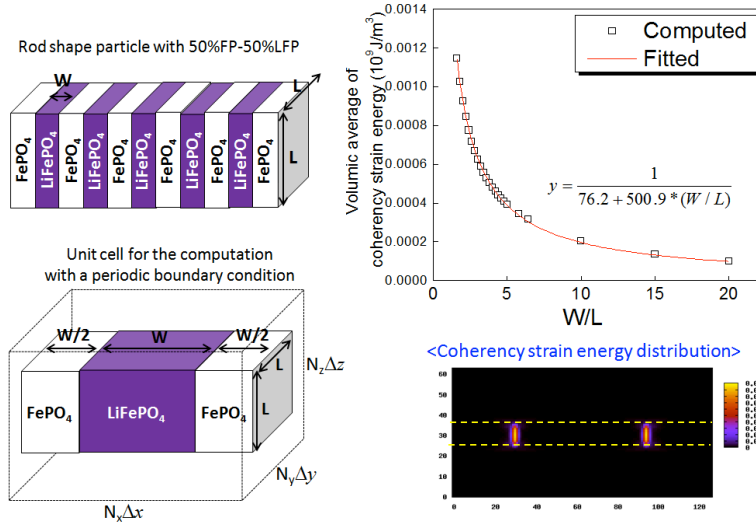


Figure 4. Parametric study of coherency strain energy in a rod shape particle

IV. Future directions

- **Developing the computational model for computing electrical potential near the interface**

To compute the distribution of electrical potential in electrode, electrolyte, and interface between the two phases is another major effort which should be done for charge transport modeling. The electrical potential profile is controlled by the ionic current in electrolyte and electronic current in an electrode. The potential at the interface is determined by the electrochemical reaction. Since the relaxation of the

electrical potential is much faster than the diffusional processes, we assume the steady state of the electrical current. By employing the smoothed boundary method [1], the following mathematical formula could be proposed:

$$\vec{\nabla} \cdot [\varphi \{ \kappa(\psi_1, \psi_2) \vec{\nabla} \Phi + zFD(\psi_1, \psi_2) \vec{\nabla} c \}] + \vec{\nabla} \varphi \cdot \vec{j}_e = 0 \quad (5)$$

where k is the electrical conductivity, Φ is the electrical potential, and D is the diffusivity of ions. By imposing the boundary condition ($\vec{j}_e \cdot \frac{\vec{\nabla} \psi_1}{|\vec{\nabla} \psi_1|} = j_{bv}$ & $\vec{j}_e \cdot \frac{\vec{\nabla} \psi_2}{|\vec{\nabla} \psi_2|} = -j_{bv}$), the final form of the equation becomes:

$$\vec{\nabla} \cdot [\varphi \{ \kappa(\psi_1, \psi_2) \vec{\nabla} \Phi + zFD(\psi_1, \psi_2) \vec{\nabla} c \}] + 2\psi_1 |\vec{\nabla} \psi_1| j_{bv} - 2\psi_2 |\vec{\nabla} \psi_2| j_{bv} = 0 \quad (6)$$

To numerically solve Eq. (6), the Fourier-spectral iterative perturbation method [3, 4] can be also applied as the case of mechanical equilibrium equation.

• Integration of the computational models and solvers

The complete capability of mesoscale modeling can be established by integrating the developed components explained above as shown in Fig. 5. The integrated framework will enable the computer simulations of charge/discharge process, coupled microstructure evolution during the process to determine the optimum condition or architecture to maximize the performance of batteries.

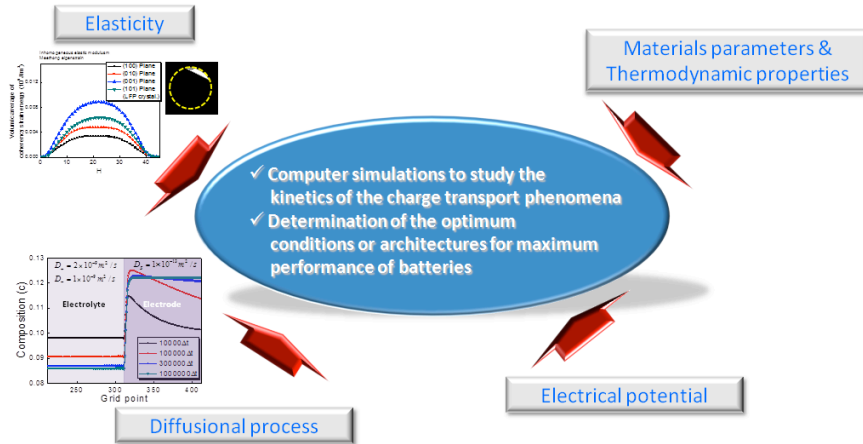


Figure 5. Integration of essential components of the mesoscale modeling of charge transport phenomena

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